

AU-A-67711/90

<p>91-218577/30 NIPPON SHOKUBAI CO LTD A41 D15 E17 02.12.89-JP-312289 (+JP-312288) (04.04.91) CO2-01/74 Treatment of waste water from (meth)acrylic acid prodn. plant - comprises subjecting to wet oxidn. in presence of solid catalyst under specified conditions continued supply of molecular oxygen contg. gas CY1-075378</p>	<p>JAPC 02.12.89 *AU 9067711-A CO2-01/74</p>
<p>resulting from this treatment is reclaimable as the service water from the (meth)acrylic acid prodn. plant.</p>	<p>The solid catalyst has as a carrier component an oxide contg. titanium and a catalytically active component formed of either a opd. of at least one metal selected from Mn, Fe, Co, Ni, W, Cu, Ce and Ag or a metal selected from Pt, Pd, Rh, Ru and Ir. The carrier accounts for 75-99.95 wt.% and the catalytically active component for 25-0.05 wt.%. (The catalytically active component is esp. a metal selected from Pt, Rh, Ru and Pd and the metal accounts for 0.1-5 wt.% of the catalyst). The carrier is at least one oxide selected from titania, titania silice and titania zirconia (esp. 20-90 mol % titania and 80-10 mol.% zirconia).</p>
<p>PREFERRED COMPONENTS</p>	<p>PREFERRED EMBODIMENT</p>
<p>The wet oxidn. reaction vessel is packed with the solid catalyst and possesses heat-exchange capacity.</p>	<p>The supply of molecular oxygen-contg. gas is carried out so that the actual linear velocity of the gas in the catalyst bed is 0.6-20 cm/sec.</p>
<p>The waste water from the (meth)acrylic acid prodn. plant.</p>	<p>The waste water from the (meth)acrylic acid prodn. plant and contg. acetic acid and aldehydes. The water</p>
<p>USE/ADVANTAGE</p>	<p>The method provides for efficient and lasting treatment of the waste water emanating from a meth acrylic acid prodn. plant and contg. acetic acid and aldehydes. The water</p>

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acid prodn. plant contains acetic acid in a concn. of 0.04-20 wt. % and aldehydes in a combined concn. of 0.02-4 wt. %. The waste gas from the prodn. plant has had 50-100% of aldehydes already oxidised at a position of 30% of the length of the catalyst bed from the inlet side.

#### CLAIMED PRODUCTION

The method for the production of (meth)acrylic acid comprises subjecting a feed gas contg. an olefin (3-4C) to gas phase catalytic oxidn. causing the resultant oxidised gas to be absorbed in water by direct contact, separating the (meth)acrylic acid from the aq. soln. of the oxidised gas and supplying the waste water to above treatment and cycling the purified waste water to a step for the absorption of the gas produced by oxidn., thereby effecting absorption of the produced gas of oxidn.

#### EXAMPLE

An appts. constructed as specified was used for treating waste water from an acrylic acid prodn. plant. The reaction vessel had 20 reaction tubes, each measuring 50 mm in inside dia. and 10m in length, housed in a barrel. The reaction tubes were filled with catalyst pellets (having 0.5wt. % of Pt deposited on a carrier of titanium-siliconium composite oxide) measuring 5mm in ave. dia. and 6mm in length to give

a catalyst bed 6m in overall length. An air dispersing plate was installed below the reaction tubes.

The waste water from an acrylic acid prodn. plant having a compen. acetic acid (2.1 wt. %), acrylic acid (0.4 wt. %), HCHO (1.5 wt. %), other organic substances (0.1 wt. %) and water 95.1 wt. % was delivered via a line in combination with the air delivered via another line at respective flow volumes of 60 litres/hr and 9600 N litres/hr per reaction tube and subjected to wet oxidn. at a reaction temp. of 250°C under a reaction pressure of 75 Kg/cm<sup>2</sup>G. The compen. of the treated water was acetic acid (20 ppm) and no other components detected. The efficiency of the treatment was almost 100%. (42pp1917HMDwgNo0/8).

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# COMPLETE SPECIFICATION

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## TO BE COMPLETED BY APPLICANT

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Complete Specification for the invention entitled:

## METHOD FOR TREATMENT OF WASTE WATER FROM (METH)ACRYLIC ACID PRODUCTION PLANT

The following statement is a full description of this invention, including the best method of performing it known to us:

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This invention relates to a method for the treatment of the waste water from a (meth)acrylic acid production plant for purification thereof by wet oxidation in the presence of a solid catalyst. More particularly, it relates to a method for the purification of the waste water containing acetic acid and aldehydes from a plant producing acrylic acid by the gaseous phase catalytic oxidation of propylene and/or acrolein or the waste water from a plant producing methacrylic acid by the gas phase catalytic oxidation of isobutylene and/or t-butyl alcohol, which purification is carried out in the presence of a solid catalyst to effect wet oxidation of the organic substances present in the waste water under continued supply of a gas containing molecular oxygen and consequent conversion of the greater part of the organic substances into harmless compounds such as carbon dioxide and water and eventual purification of the waste water. Further, it relates to a method for the production of (meth)acrylic acid combining a purification process of the waste water.

#### Description of the Prior Art:

Generally, as methods for the treatment of the waste water from a (meth)acrylic acid production plant, the activated sludge method and the catalytic combustion method have been known to the art. As universally known, the activated sludge method has the disadvantage that it requires a long time for decomposition of organic substances and, what is more, requires the waste water to be diluted to a concentration suitable for the growth of algae and bacteria and, consequently, entails inevitable use of an unduly large area for the installation of facilities for the treatment with activated sludge. Particularly, when the waste water from a (meth)acrylic acid production plant is to

be treated by the activated sludge method, since the waste water contains aldehydes such as formaldehyde and acetaldehyde which are poisons to organisms, the problem arises that the waste water is required to be diluted in a large number of multiples, the efficiency of treatment with activated sludge declines in stability, the cost of waste water treatment increases and, at the same time, the treatment itself is difficult. The acetic acid entrained in the waste water is held to be a substance suffering from inferior efficiency of biodecomposition and, under the restrictions for environmental preservation, is required to be decomposed to a large extent. The activated sludge method, however, has the problem mentioned above.

When the direct combustion method is applied to the waste water from a (meth)acrylic acid production plant, it necessitates use of a combustion aiding agent in a large volume and incurs a large cost of treatment because the waste water contains organic substances in a low concentration. Further, since this waste water contains low boiling organic substances as main components, the concentration to be performed as a pretreatment is not easy to carry out.

An object of this invention, therefore, is to provide a method for efficient and lasting treatment of the waste water emanating from a (meth)acrylic acid production plant and containing acetic acid and aldehydes.

Another object of this invention is to provide a method for the treatment of the waste water, which method has the advantage that the water resulting from this treatment is reclaimable as the service water for the (meth)acrylic acid production plant.

#### SUMMARY OF THE INVENTION

These objects are accomplished by a method for the purification of the waste water discharging from a (meth)acrylic acid production plant and containing acetic acid and aldehydes by the use of a wet oxidation reaction

vessel packed with a solid catalyst at temperature not exceeding 370°C under a pressure enough for the waste water to retain a liquid phase under continued supply of a gas containing molecular oxygen to effect wet oxidation of organic substances entrained by the waste water.

These objects are also accomplished by a method for the production of (meth)acrylic acid, which comprises subjecting a feed gas containing an olefin of 3 or 4 carbon atoms to gas phase catalytic oxidation, causing the resultant oxidized gas to be absorbed in water by direct contact therewith, separating (meth)acrylic acid from the resultant aqueous solution of said oxidized gas, supplying the resultant waste water containing acetic acid and aldehydes to a wet oxidation reaction vessel packed with a solid catalyst and operated at a temperature not exceeding 370°C under a pressure enough for said waste water to retain a liquid phase under continued supply of a molecular oxygen-containing gas thereby purifying said waste water by wet oxidation of organic substances entrained by said waste water, and cycling the purified waste water to a step for the absorption of the gas produced by oxidation thereby effecting absorption of said produced gas of oxidation.

In the present invention, since the waste water from the (meth)acrylic acid production plant is oxidized to a high extent, the water resulting from the treatment can be reclaimed as the service water for the plant. The plant for producing acrylic acid by the gas phase catalytic oxidation of propylene or the plant for producing methacrylic acid by the gas phase catalytic oxidation of isobutylene and/or t-butyl alcohol is structurally divided broadly into two systems, i.e. the oxidation system and the purification system. Water is used at various sites in the component devices of the plant. Among other devices, the (meth)acrylic acid absorption tower and the distillation tower consume water in large volumes. Thus, the recyclic use of the water resulting from the treatment of wet

oxidation allows a generous reduction in terms of utility and a decrease in the cost of (meth)acrylic acid production.

5 The treated water of this invention resulting from the wet oxidation of the waste water from the (meth)acrylic acid production plant is characterized by containing acetic acid in a very minute amount. It has been found that since this treated water can be used in the (meth)acrylic acid production plant without exerting any adverse effect on the plant operation, the method of this invention allows  
10 adoption of a closed system for the (meth)acrylic acid production plant. The incorporation of the waste water treatment system contemplated by this invention enables the (meth)acrylic acid production plant to be operated without entailing emanation of waste water.

15 The waste water from a (meth)acrylic acid production plant contains organic substances in a too high concentration to be effectively treated with activated sludge and, therefore, must be diluted to many multiples of its volume to allow the treatment. For the treatment of  
20 this waste water by combustion, the concentration of such organic substances in the waste water is too low. This treatment, therefore, entails heavy consumption of an auxiliary fuel. In contrast, the wet oxidation according with this invention is highly suitable for the treatment of  
25 the waste water from a (meth)acrylic acid production plant because it allows the waste water to be directly treated with high efficiency.

Generally, when the acetic acid concentration in the absorption water is increased in the (meth)acrylic acid  
30 collection device, the acetic acid concentration in the waste gas containing the unaltered feed gas such as olefin and being returned to the raw material system is proportionately increased possibly to the extent of exerting an adverse effect on the catalyst used for the production of  
35 (meth)acrylic acid. In contrast, in the treatment by wet oxidation, since the treated water contains substantially no

acetic acid, it can be cyclically utilized as an absorption water, with the result that the efficiency of production of (meth)acrylic acid will be improved.

#### BRIEF DESCRIPTION OF THE DRAWINGS

5 Figs. 1 to 4 are flow sheets shown an outline of a method for the treatment of the waste water from a (meth)acrylic acid production plant,

Fig. 5 is a flow sheet shown an outline of a method for the production of acrylic acid and

10 Fig. 5 is a flow sheet shown an outline of a method for the production of methacrylic acid.

#### EXPLANATION OF THE PREFERRED EMBODIMENT

15 In accordance with this invention, the desire to complete a (meth)acrylic acid production plant incapable of issuing harmful waste substances can be fulfilled because the greater part of such organic substances as acetic acid and aldehydes entrained by the waste water from a (meth)acrylic acid production plant can be converted into such harmless substances as carbon dioxide and water by 20 subjecting the waste water to the treatment of wet oxidation using a solid catalyst.

25 As a method for performing the treatment of wet oxidation, the Zimmerman method which has no use for a catalyst has been known to the art. Numerous methods using various oxidation catalysts for the acceleration of reaction velocity have been proposed. The method of treatment resorting to wet oxidation, however, has never been applied to the waste water emanating from a (meth)acrylic acid production plant and consequently entraining acetic acid and aldehydes. 30

35 The waste water from the acrylic acid production plant which is subjected to the treatment of the present invention contains acetic acid and aldehydes. Though this invention does not discriminate the waste water on account of its particular composition, the waste water generally has the following composition, for example.



Acetic acid	0.04 to 10% by weight
Acrylic acid	0.02 to 3% by weight
Formaldehyde	0.04 to 4% by weight
Other organic substances	0 to 2% by weight
Water	Balance

The waste water from the methacrylic acid production plant which is subjected to the treatment of the present invention contains acetic acid and aldehydes. Though this invention does not discriminate this waste water on account of its particular composition, the waste water generally has the following composition, for example.

Acetic acid	0.1 to 20% by weight
Acrylic acid	0.02 to 3% by weight
Methacrylic acid	0.04 to 4% by weight
Aldehydes	0.02 to 3% by weight
Other organic substances	0 to 3% by weight
Water	Balance

As respects the decomposition of acetic acid, among other defiling substances in the waste water from a (meth)acrylic acid production plant, the conventional method of wet oxidation suffers from inferior efficiency of treatment and consequently requires the use of a secondary treatment and a tertiary treatment. In contrast, the method of wet oxidation by the use of a catalyst of this invention allows the treatment to be performed with high efficiency and permits compaction of the system and reduction in the cost of treatment.

The supply of a gas containing molecular oxygen is preferable to be carried out so that the actual linear velocity of the gas in the catalyst bed falls in the range of 0.6 to 20 cm/sec, preferably 1 to 12 cm/sec. The term "actual linear velocity of gas" refers to the magnitude found by dividing the flow volume of the gas in the catalyst bed at the existent temperature and pressure by the cross-sectional area of the catalyst bed (in the plane perpendicular to the vertical axis).

By keeping the actual linear velocity of the gas in the range defined above, it is made possible to improve the gas-liquid agitation by the gas within the catalyst bed, accelerate the dissolution of oxygen in the liquid phase and, at the same time, accelerate the separation of carbon dioxide from the liquid phase, and enhance notably the efficiency of decomposition of acetic acid which is deficient in reactivity. It is further made possible to prevent the pressure loss in the catalyst bed from being aggravated.

Particularly, when the waste water from a (meth)acrylic acid production plant happens to contain 0.04 to 20% by weight of acetic acid and 0.02 to 4% by weight of aldehydes, the method of this invention is used advantageously because it facilitates the control of reaction and enhances the efficiency of wet oxidation.

Further, the efficiency with which the removal at the outlet of the catalyst bed of sparingly oxidizable acetic acid is attained can be enhanced by suitably setting the conditions of reaction temperature, pressure, and space velocity of liquid (LHSV) to 50 to 100% of that the aldehydes in the waste water from a (meth)acrylic acid production plant are oxidized at the position of 30% of the length of the catalyst bed from the inlet side thereof. Further, the aldehydes are oxidized competitively on the point of catalytic activity because the oxidation of acetic acid is promoted in consequence of the decrease of aldehydes.

The catalyst to be used in the present invention is preferable to use a titanium-containing oxide as a carrier therefor.

To be more specific, a catalyst obtained by depositing the metal of such a catalytically active element as manganese, iron, cobalt, nickel, tungsten, copper, cerium, silver, gold, platinum, palladium, rhodium, ruthenium, or iridium or a compound of the catalytically

active element insoluble in or sparingly soluble in water on a carrier of titania, titania-silica, or titania-zirconia is used herein.

The catalyst is composed of 75 to 99.95%, preferably 85 to 99.9%, by weight of the carrier and 25 to 0.05%, preferably 15 to 0.1%, by weight of the metal or compound of the catalytically active element mentioned above. The compound of a catalytically active element selected from the group consisting of manganese, iron, cobalt, nickel, tungsten, copper, cerium, and silver is used in an amount in the range of 0 to 15% by weight as compound, whereas the compound of a catalytically active element selected from the group consisting of platinum, palladium, rhodium, ruthenium, and iridium is used in an amount in the range of 0 to 5%, preferably 0 to 3 %, by weight. (It is provided, however, that a mixture of two such compounds is used in an amount in the range of 0.1 to 15% by weight.) Among other catalysts conceivably usable herein, a catalyst having deposited on the carrier at least one metal selected from the group consisting of platinum, palladium, rhodium, and ruthenium in the range of 0.1 to 5 % by weight, preferably 0.1 to 3% by weight is used particularly advantageously. A catalyst having a metal of the aforementioned platinum family deposited on a titania-zirconia carrier proves to be more preferable. Particularly when this catalyst uses a binary composite oxide comprising of 20 to 90 mol% of titania and 80 to 10 mol% of zirconia, it exceptionally suits the treatment of the waste water from a (meth)acrylic acid production plant which contains aldehydes and acetic acid because it excels in activity, resistance to hot water, acidproofness, and durability.

The catalyst may be formed in any of the shapes known to the art such as, for example, pellets, beads, honeycombs, and rings.

The reaction vessel to be used in the present invention may be any of the various known types such as a

single-tube cylinder type reaction vessel of the adiabatic system and a reaction vessel furnished with a heat-exchange functionality. In the two particular reaction vessels mentioned above, the reaction vessel endowed with the heat-exchange ability proves to be more preferable than the other reaction vessel.

The conventional method of wet oxidation prefers the single-tube cylinder type reaction vessel not endowed with a heat-exchange ability to the other reaction vessel. The reaction vessel of this type is incapable of treating highly concentrated waste water because it does not contemplate removing the heat of reaction arising from the decomposition of the waste water. Even in the waste water from the (meth)acrylic acid production plant which is subjected to the treatment by the method of this invention, the concentration of defiling substances in the water varies in a wide range of 0.1 to 20% with the variation such as of operating conditions. When the waste water of a high concentration is actually supplied, the reaction fails to proceed because the amount of heat to be generated is so large that the temperature of the liquid within the reaction column is conspicuously elevated, and the water is wholly passed into the liquid phase. In this case, the amount of the heated generated must be controlled by diluting the waste water. The dilution of the waste water is nothing desirable because it causes an increase in the amount of the treated water.

The treatment under discussion manifests an outstanding effect by using a heat-exchanger type reaction vessel as a reaction device possessed of a construction capable of sufficient removal of the heat of reaction.

The use of this heat-exchanger type reaction vessel enables the treatment to be readily performed without requiring application of any undue pressure because it permits thorough removal of the heat even when the waste water from a (meth)acrylic acid production plant happens to

have a high concentration. Even when the waste water has a low concentration and the amount of heat to be generated is small, the necessity for unduly heightening the reaction pressure with consideration to the possible elevation of the liquid temperature due to the generation of heat is obviated. Further, the amount of the heat to be removed can be increased or decreased and consequently controlled with high accuracy by adjusting the amount of a heat transfer medium within the cooling heat-exchanger proportionately to the concentration and amount of the waste water from the (meth)acrylic acid production plant.

Further, the heat of reaction recovered within the reaction vessel can be transferred through the agency of a heat transfer medium to a steam-generating boiler and reclaimed therein in the form of steam and utilized efficiently for preheating the waste water. This reclamation of the heat of reaction permits a generous reduction in the operating cost of the system, the cost of equipment, etc.

Among other heat-exchanger type reaction vessels, the shell-and-tube heat-exchanger type reaction vessel proves to be particularly preferable. This type permits the reaction vessel to be simplified in construction and facilitates the design and maintenance of the reaction vessel and, at the same time, decreases the number of component parts otherwise requiring use of a highly corrosionproof material by limiting the passage of the waste water to the interiors of the inner tubes and cuts the cost of the reaction vessel (Fig. 1).

In the method of this invention, it is desirable to use a shell-and tube heat-exchanger type reaction vessel of the kind possessed of a gas feeding device furnished in the lower part of each of the reaction tubes (inner tubes) with a gas feeding nozzle and to keep the pressure loss in each of the gas feeding nozzles at a level not exceeding  $0.05 \text{ kg/cm}^2$ , preferably falling in the range of  $0.1$  to  $1 \text{ kg/cm}^2$ .

The term "pressure loss in each gas feeding nozzle" as used herein is meant to refer to the magnitude of pressure difference which occurs under the flow of gas between the gas feeding manifold to the nozzle and the nozzle outlet.

5 The molecular oxygen-containing gases which are usable herein include air, pure oxygen, and oxygen-enriched air, for example.

10 The shell-and-tube heat-exchanger type reaction vessel according with this invention, by having gas feeding nozzles disposed one each in the lower parts of the reaction tubes, is enabled to supply the molecular oxygen-containing gas in an equal amount to each of the reaction tubes. As the result, the waste water, by being entrained by the gas emanating from the gas feeding nozzles, is enabled to be  
15 supplied in an equal amount to each of the reaction tubes. In order for the gas to be supplied in an equal amount from the gas feeding nozzles to the reaction tubes, the pressure loss in each of the nozzles is required to exceed  $0.05 \text{ kg/cm}^2$  and preferable to fall in the range of  $0.05$  to  $2 \text{ kg/cm}^2$ , preferably  $0.1$  to  $1 \text{ kg/cm}^2$ . If the pressure loss is less than  $0.05 \text{ kg/cm}^2$ , the flow volumes of gas emanating from the individual nozzles are varied possibly to the extent of giving rise to large drifts and consequently rendering it difficult to supply the gas in an equal amount  
20 to the reaction tubes.

25 The differences in pressure loss among the plurality of nozzles of the gas feeding device in this invention are required to be within 40% and desired to be within 25%. If the differences in pressure loss among the nozzles exceed 40%, the gas is not easily supplied in an equal amount to the reaction tubes and, as the result, the waste water is not entrained in an equal amount. Thus, the gas and the waste water are both liable to entail the phenomenon of drifting and, consequently, induce a decline in the  
30 efficiency of treatment.

The nozzles of the gas feeding device of the present invention are only required to have a construction capable of imparting a pressure difference to the passing gas. The supply of a gas to the nozzles of the gas feeding device may be effected by the use of radially disposed pipes, annular pipes, or small air reservoir drums (Fig. 3).

In the present invention, the wet oxidation is carried out more effectively by using a shell-and-tube heat-exchanger type reaction vessel in the first stage of treatment and a single tube cylinder type reaction vessel in the second stage. This is because in the reaction of wet oxidation of the present invention, the greater part of the reaction is produced at the site close to the hot part of the reaction vessel and the generation of the heat of reaction is concentrated also at this site, according to the information acquired by the present invention. To be specific, the reaction vessel endowed with a heat-exchange ability is used in the first stage which dictates removal of the heat of reaction and the single tube cylinder type reaction vessel destitute of a heat-exchange ability is used in the second stage which admits the waste water emanating from the heat-exchange type reaction vessel and consequently possessing a small amount of heat and allows the remainder of the reaction to proceed adiabatically. By constructing the system as described above, the shell-and-tube heat-exchange type reaction vessel can be reduced in size and consequently the cost of equipment can be lowered (Fig. 2).

Now, the embodiment of this invention will be described below with reference to the accompanying drawings.

Fig. 1 is a schematic diagram illustrating an apparatus for the treatment of the waste water from a (meth)acrylic acid production plant as one embodiment of this invention. First, the waste water delivered from a (meth)acrylic acid production plant via a line 13 is forwarded by a waste water feeding pump 7 to a heat-exchanger 5, pre-heated therein, and supplied thence to a

reaction vessel 1. This reaction vessel 1 has a plurality of inner tubes housed inside a barrel 12. A dispersing plate (not shown) is disposed, when necessary, below the reaction tubes. In the meantime, the molecular oxygen-containing gas delivered via a line 14 is compressed by a compressor 6 and then supplied via a line 19 to reaction tubes 11 inside the reaction vessel 1. The compressed molecular oxygen-containing gas may be otherwise forwarded via a line 20 and supplied in company with the waste water to a heat-exchanger 5. Alternatively, part of the compressed molecular oxygen-containing gas may be forwarded via the line 19 and the remainder thereof supplied via the line 20 to the reaction vessel 1. A heat transfer medium is supplied by a circulation pump 3 via a line 15 to the space enclosing the inner tubes (reaction tubes) 11 inside the reaction vessel 1 and used therein for the removal of the heat of reaction generated during the course of reaction. Then, the heat transfer medium is discharged via a line 16 into a heat-exchanger 4, wherein it exchanges heat with the cooling water delivered thereto via a line 17 to effect cooling of the heat transfer medium and recovery of the heat of reaction therefrom. The waste water treated by the reaction vessel 1 is discharged via a line 18, cooled by the heat-exchanger 5, and then supplied to a gas-liquid separator 8, wherein it is separated into a harmless gas and water. In the gas-liquid separator 8, the liquid level is maintained at a constant height by causing a liquid level controller LC to detect the liquid level and a liquid level control valve 9 to actuate itself accordingly and the inner pressure is maintained at a constant magnitude by causing a pressure controller PC to detect the existent pressure and a pressure control valve 10 to actuate itself accordingly. Optionally, the treated water withdrawn through the liquid level control valve 9 via a line 21 may be used as the service water for absorption of (meth)acrylic acid in a



(meth)acrylic acid absorption tower of a (meth)acrylic acid production plant.

Fig. 2 is a schematic diagram illustrating another embodiment of this invention using a shell-and-tube heat-exchanger type reaction vessel in the first stage and a single tube cylinder type reaction vessel in the second stage. A first reaction vessel 21a of the heat-exchanger type is identical with the reaction vessel of Fig. 1. In a second reaction vessel 21b of the single tube cylinder type, a solid catalyst is placed to fill the interior of the single tube and an insulating material 42 is placed to enclose the single tube.

First, the waste water from a (meth)acrylic acid production plant delivered via a line 33 is forwarded by a waste water feeding pump 27 to a heat-exchanger 25, pre-heated therein, and supplied thence to the first reaction vessel 21a. In the meantime, the molecular oxygen-containing gas supplied via a line 34 is compressed by a compressor 26 and then supplied into reaction tubes 31 of the first reaction vessel 21a via a line 40. The compressed molecular oxygen-containing gas, when necessary, may be forwarded via a line 39 and supplied in company with the waste water to a heat-exchanger 25. Otherwise, part of the compressed molecular oxygen-containing gas is forwarded via a line 39 and supplied to the first reaction vessel 21a.

The heat transfer medium is supplied by a circulation pump 23 via a line 35 to the space enclosing the inner tubes (reaction tubes) 31 of the first reaction vessel 21a, used therein for the removal of the heat of reaction generated during the course of reaction, then discharged via a line 36, supplied to the heat-exchanger 44, and caused therein to exchange heat with the cooling water delivered via a line 37 and effect cooling of the heat transfer medium and recovery of the heat of reaction therefrom. The waste water treated by the first reaction vessel 21a is supplied to the second reaction vessel 21b, treated therein,

discharged via a waste water line 38, cooled by the heat-exchanger 25, and then supplied to a gas-liquid separator 28, wherein it is separated into a harmless gas and water. In the gas-liquid separator 28, the liquid level is maintained at a constant height by causing a liquid level controller LC to detect the existent liquid level and a liquid level control valve 29 to actuate itself accordingly and, at the same time, the pressure therein is maintained at a constant magnitude by causing a pressure controller PC to detect the existent pressure and a pressure control valve 30 to actuate itself accordingly. Optionally, the treated water withdrawn through a liquid level control valve 29 via a line 41 may be used as the service water for absorption of (meth)acrylic acid in a (meth)acrylic acid absorption column of a (meth)acrylic acid production plant.

Fig. 3 is a schematic diagram illustrating one embodiment of the shell-and-tube heat-exchanger 49 to be used in the present invention. A solid catalyst is placed to fill reaction tubes 51 of the shell-and-tube heat-exchanger 49. The waste water from a (meth)acrylic acid production plant is supplied via a line 53 to this reaction vessel 49. In the meantime, the molecular oxygen-containing gas delivered via a line 59 is supplied through nozzles 60. A heat transfer medium is supplied by a circulation pump 48 to the space enclosing the reaction tubes 51 of the reaction vessel 49, used therein to cool the reaction vessel, discharged via a line 55 to a heat-exchanger 54, and caused therein to exchange heat with the cooling water supplied via the line 57.

Fig. 4 is a schematic diagram illustrating yet another embodiment of this invention. The apparatus of this embodiment is identical with that of Fig. 1, except that a single tube cylinder type reaction vessel 61 is used in the place of the shell-and-tube heat-exchanger type reaction vessel and the device for the recovery of the heat of reaction is omitted. In Fig. 4, the reference numerals

which are the sum of those of the parts of Fig. 1 plus 60 denote identical parts.

Fig. 5 is a flow chart schematically illustrating a method for the production of acrylic acid incorporating therein a step for the treatment of waste water by wet oxidation. The reaction product gas resulting from the gas-phase catalytic oxidation of propylene and/or acrolein with a molecular oxygen-containing gas is introduced via a line 91 into a acrylic acid collection device 101. In this collection device 101, the gas is condensed by sudden cooling so that the greater part of the acrylic acid and acetic acid is converted into an aqueous solution. The part of the gas which has escaped the condensation is absorbed and collected in the upper part of the collection device 101 by the cooling absorption water containing a polymerization inhibitor and supplied via a line 92. The aqueous acrylic acid solution is withdrawn from the lower part of the collection device 101 via a line 93. The waste gas arising from the treatment is discharged from the top of the collection device 101 via a line 94.

The aqueous acrylic acid solution withdrawn via the line 93 is supplied to an azeotropic dehydration tower 102. In the azeotropic dehydration column 102, an azeotrope-forming agent is introduced through the top of the tower via a line 95 in a manner so controlled that the steam distilled through the top of the column via a line 96 assumes the form of an azeotropic mixture of water and the azeotrope-forming agent. In the meantime, acrylic acid, acetic acid, and other high-boiling substances which do not contain water or the azeotrope-forming agent are withdrawn through the bottom of the column and then treated at the step of acrylic acid reofification (not shown) and discharged thence as a finished product.

The liquid distilled through the top of the azeotropic dehydration column 102 is introduced into a separation tank 104 and separated therein into an azeotrope-

forming agent phase and a water phase. The water phase is forwarded via a line 98 to an azeotrope-forming agent recovery column 103. The azeotrope-forming agent and part of the water are distilled through the top of the column 103, forwarded via a line 99 to the separation tank 104, and recovered therein.

In the meantime, the liquid containing aldehydes and acetic acid and not containing the azeotrope-forming agent is withdrawn through the bottom of the azeotrope-forming agent recovery column 103 via a line 100. Part of this liquid, when necessary, is circulated via a line 105 to the acrylic acid collection device 101 and used again as an absorption water. The remainder of the liquid is forwarded via a line 13 to the step for wet oxidation of the waste water. The reference numeral 106 stands for a feeding line for the polymerization inhibitor.

The step of wet oxidation is identical with the step illustrated in Fig. 1. Similarly, the steps illustrated in Figs. 2 to 4 may be incorporated in the place of the step illustrated in Fig. 1. The waste water treated at the step mentioned above is circulated via a line 107 to the acrylic acid collection device 101 and utilized as the absorption water.

The waste water discharged via the line 100 is purged of organic components by wet oxidation with the solid catalyst. By adopting the wet oxidation as means of purification for the treatment of waste water in the azeotrope-forming agent recovery column 103, a closed and integrated system can be materialized which covers the production of acrylic acid and the treatment of the waste water arising from the production. Further, the operation to be performed for the production and the conditions involved therein are easily altered because the treatment of waste water can be regulated to suit the prevalent amount and composition of the waste water which are susceptible to variations in the load of the operation.

The treated water which has been purified by the wet oxidation can be utilized as the absorption water in the acrylic acid collection device 101 because it does not contain any substance which exerts an adverse effect upon acrylic acid. This reclamation of the treated water serves the purpose of generously decreasing the consumption of service water and consequently lowering the cost of production of acrylic acid.

Fig. 6 is a flow chart schematically illustrating a method for the production of methacrylic acid incorporating therein a step for the treatment of waste water by wet oxidation. The reaction product gas resulting from the gas-phase catalytic oxidation of isobutylene and/or t-butyl alcohol with a molecular oxygen-containing gas is introduced via a line 111 into a methacrylic acid condensation column 121. In this condensation column 121, the gas is condensed by sudden cooling so that the greater part of the methacrylic acid and acetic acid is converted into an aqueous solution. The part of the gas which has escaped the condensation is absorbed and collected in the upper part of the condensation column 121 by the cooling absorption water containing a polymerization inhibitor and supplied via a line 112. The aqueous methacrylic acid solution is withdrawn from the lower part of the condensation column 121 via a line 113. The waste gas arising from the treatment is discharged from the top of the condensation column 121 via a line 114.

The aqueous methacrylic acid solution withdrawn via the line 113 is supplied to a methacrylic acid extraction column 122, while a solvent for extracting methacrylic acid is charged to the extraction column 122 from the under portion via a line 128, and both are counter currently contacted each other, methacrylic acid is extracted into a solvent phase and discharged via a line 116, and an aqueous phase is discharged via a line 117. The solvent phase after extraction is distilled in a solvent separation column 124,

and the solvent is recovered and circulated to the methacrylic acid extraction column 122. On the contrary, crude methacrylic acid is discharged via a line 115 to prepare a product via a methacrylic acid purification step (not shown).

On the other hand, aqueous phase after extracting methacrylic acid is introduced to a solvent recovery column 123 to be distilled via a line 117, the solvent is charged to a methacrylic acid extraction column 122 via lines 119 and 128, a liquid containing aldehydes and acetic acid in the aqueous phase is discharged from the bottom of the solvent recovery column 123 via a line 120. Part of this liquid, when necessary, is circulated via a line 125 to the methacrylic acid condensation column 121 and used again as an absorption water. The remainder of the liquid is forwarded via a line 13 to the step for wet oxidation of the waste water. The reference numeral 126 stands for a feeding line for the polymerization inhibitor.

The step of wet oxidation is identical with the step illustrated in Fig. 1. Similarly, the steps illustrated in Figs. 2 to 4 may be incorporated in the place of the step illustrated in Fig. 1. The waste water treated at the step mentioned above is circulated via a line 127 to the methacrylic acid condensation column 121 and utilized as the absorption water.

The waste water discharged via the line 120 is purged of organic components by wet oxidation with the solid catalyst. By adopting the wet oxidation as means of purification for the treatment of waste water in the solvent recovery column 123, a closed and integrated system can be materialized which covers the production of methacrylic acid and the treatment of the waste water arising from the production. Further, the operation to be performed for the production and the conditions involved therein are easily altered because the treatment of waste water can be regulated to suit the prevalent amount and composition of

the waste water which are susceptible to variations in the load of the operation.

The treated water which has been purified by the wet oxidation can be utilized as the absorption water in the methacrylic acid condensation column 121 because it does not contain any substance which exerts an adverse effect upon methacrylic acid. This reclamation of the treated water serves the purpose of generously decreasing the consumption of service water and consequently lowering the cost of production of methacrylic acid.

Now, the present invention will be described more specifically below with reference to working examples.

#### Example 1

An apparatus constructed as illustrated in Fig. 1 was used for treating the waste water from an acrylic acid production plant. A reaction vessel 1 had 20 reaction tubes (inner tubes) 11 each measuring 50 mm in inside diameter and 10 m in length housed in a barrel. The reaction tubes 11 were filled with catalyst pellets (having 0.5% by weight of Pt deposited on a carrier of a titanium-zirconium composite oxide) measuring 5 mm in average diameter and 6 mm in length to give rise to a catalyst bed 8 m in overall length. An air dispersing plate (not shown) was installed below the reaction tubes.

The waste water from an acrylic acid production plant (having a composition as shown in Table 1) delivered via a line 13 was supplied in combination with the air delivered via a line 14 to the reaction vessel 1 at respective flow volumes of 60 liters/hr and 9,600 Nliters/hr per reaction tube (namely at respective total flow volumes of  $1.2 \text{ m}^3/\text{hr}$  and  $192 \text{ Nm}^3/\text{hr}$ , with actual linear velocity of gas at 3.4 cm/sec) and subjected to wet oxidation at a reaction temperature of  $250^\circ\text{C}$  under a reaction pressure of  $75 \text{ kg/cm}^2\text{G}$ . The composition of the treated water extracted from a line 21 and the efficiency of treatment were as shown in Table 1.

Table 1

	Waste water from acrylic acid production plant <u>(% by weight)</u>	Treated water <u>(ppm)</u>	Efficiency of treatment (%)
Acetic acid	2.1	20	99.9
Acrylic acid	0.4	ND	100
Formaldehyde	1.5	ND	100
Other organic substances	0.1	ND	100
Water	95.1	-	-

ND: not detectable

#### Example 2

A treating apparatus constructed as illustrated in Fig. 1 was used for treating the waste water from a methacrylic acid production plant. A reaction vessel 1 had 20 reaction tubes (inner tubes) 11 each measuring 50 mm in inside diameter and 10 m in length housed in a barrel. The reaction tubes 11 were filled with catalyst pellets (having 0.5% by weight of Pt deposited on a carrier of a titanium-zirconium composite oxide) measuring 5 mm in average diameter and 6 mm in length to give rise to a catalyst bed 8 m in overall length. An air dispersing plate (not shown) was disposed below the reaction tubes.

The waste water from a Methacrylic acid production plant (having a composition shown in Table 2) delivered via a line 13 was supplied in combination with the air delivered via a line 14 to the reaction vessel 1 at respective flow volumes of 80 liters/hr and 20,800 Nliters/hr per reaction tube (namely at respective total feed volumes of 1.6 m<sup>3</sup>/hr and 416 Nm<sup>3</sup>/hr, with actual linear velocity of gas at 7.4 cm/sec) and subjected to wet oxidation at a reaction



temperature of 25°C under a reaction pressure of 75 kg/cm<sup>2</sup>G. The composition of the treated water extracted from a line 21 and the efficiency of treatment were as shown in Table 2.

Table 2

	Waste water from methacrylic acid production plant (% by weight)	Treated water (ppm)	Efficiency of treatment (%)
--	---	---------------------------	--------------------------------

Acetic acid	4.2	100	99.8
Acrylic acid	0.3	ND	100
Methacrylic acid	0.5	ND	100
Aldehydes	1.0	ND	100
Other organic substances	0.5	ND	100
Water	93.5	-	-

### Example 3

The waste water from an acrylic acid production plant was treated by following the procedure of Example 1, except that the type of the reaction vessel was changed to a single tube cylinder type reaction vessel of an adiabatic construction (measuring 220 mm in inside diameter and 10 m in height and having a catalyst bed 8 m in height) illustrated in Fig. 4 and amount of the waste water changed to 0.9 m<sup>3</sup>/hr amount of air changed to 112 Nm<sup>3</sup>/hr (via a line 79) and the actual linear velocity of gas changed to 2.1 cm/sec. The results were as shown in Table 3.

### Example 4

The procedure of Example 3 was repeated, except that the flow volume of the air was changed to 216 Nm<sup>3</sup>/hr (via a

line 80) and the actual linear velocity of gas to 4.0 cm/sec. The results were as shown in Table 3.

Table 3

Example 3

Example 4

	Waste water from acrylic acid production plant (% by weight)	Treated water (ppm)	Efficiency of treatment (%)	Waste water from acrylic acid production plant (% by weight)	Treated water (ppm)	Efficiency of treatment (%)
Acetic acid	1.2	20	99.8	2.0	50	99.8
Acrylic acid	0.5	ND	100	2.3	ND	100
Formaldehyde	1.3	ND	100	1.3	ND	100
Other organic substances	0.1	ND	100	0.4	ND	100
Water	96.9	-	-	94.0	-	-

# Examples 5 to 7

The waste water from an acrylic acid production plant was treated by following the procedure of Example 1, excepting the catalyst was varied. The compositions of such catalysts and the results were as shown in Table 4.

Table 4

	Example 5	Example 6	Example 7
Composition of catalyst	Rh (0.6% wt) -TZ	Ru (1.5% wt) -TZ	Pd (1.5% wt) -TiO <sub>2</sub>
Efficiency of treatment (%)			
Acetic acid	99.6	98.1	94.5
Acrylic acid	100	100	100
Formaldehyde	100	100	100
Other organic substances	100	99	98

TZ: A titanium and zirconium composite oxide carrier  
(TiO<sub>2</sub>/ZrO<sub>2</sub> = 60/40 % weight ratio)

TiO<sub>2</sub>: Titania carrier

## Example 8

When the procedure of Example 3 was repeated, except that the reaction vessel measured 500 mm in inside diameter and 3 m in height and used a catalyst bed 1.55 m in overall height, the actual linear velocity of gas was found to be 0.4 cm/sec and the efficiency of treatment of acetic acid was found to be 95.8%.

## Example 9

When the procedure of Example 4 was repeated, except that the reaction vessel measured 80 mm in inside diameter and 12 m in height and used six serially arranged catalyst beds each measuring 10 m in height, the actual linear velocity of gas was found to be 30 cm/sec and the efficiency of treatment of acetic acid was found to be 98.2%. The

pressure loss in the catalyst beds conspicuously increased to 11 kg/cm<sup>2</sup>.

#### Example 10

In the treatment of Example 3, the liquid was sampled at a position of 30% of the length of the catalyst bed from the inlet side thereof and analyzed to determine the efficiency of treatment. The efficiency was found to be 79% for acetic acid, 92% for acrylic acid, 100% for formaldehyde, and 89% for other organic substances.

#### Example 11

The waste water from an methacrylic acid production plant was treated by following the procedure of Example 2, except that the type of the reaction vessel was changed to a single tube cylinder type reaction vessel of an adiabatic construction (measuring 220 mm in inside diameter and 10 m in height and having a catalyst bed 8 m in height) illustrated in Fig. 4 and amount of the waste water changed to 1.2 m<sup>3</sup>/hr, amount of air changed to 255 Nm<sup>3</sup>/hr (via a line 79) and amount of the waste water changed to 0.9 m<sup>3</sup>/hr amount of air changed to 112 Nm<sup>3</sup>/hr (via a line 79) and the actual linear velocity of gas changed to 4.7 cm/sec. The results were as shown in Table 5.

#### Example 12

The procedure of Example 11 was repeated, except that the flow volume of the air was changed to 264 Nm<sup>3</sup>/hr (via a line 80) and the actual linear velocity of gas to 4.9 cm/sec. The results were as shown in Table 5.

Table 5

Example 11

Example 12

	Waste water from methacrylic acid production plant (% by weight)	Treated water (ppm)	Efficiency of treatment (%)	Waste water from methacrylic acid production plant (% by weight)	Treated water (ppm)	Efficiency of treatment (%)
Acetic acid	3.4	110	99.7	2.0	60	99.7
Acrylic acid	0.3	ND	100	1.4	ND	100
Methacrylic acid	0.9	ND	100	1.3	ND	100
Aldehydes	0.5	ND	100	0.5	ND	100
Other organic substances	0.2	ND	100	0.3	ND	100
Water	94.7	-	-	94.5	-	-

### Examples 13 to 15

The waste water from an acrylic acid production plant was treated by following the procedure of Example 2, excepting the catalyst was varied. The compositions of such catalysts and the results were as shown in Table 6.

Table 6

	Example 13	Example 14	Example 15
Composition of catalyst	Rh (0.6% wt) -TZ	Ru (1.5% wt) -TZ	Pd (1.5% wt) -TiO <sub>2</sub>
Efficiency of treatment (%)			
Acetic acid	99.4	96.0	91.0
Acrylic acid	100	100	100
Methacrylic acid	100	100	100
Aldehydes	100	100	100
Other organic substances	100	99	96

TZ: A titanium and zirconium composite oxide carrier  
(TiO<sub>2</sub>/ZrO<sub>2</sub> = 60/40 % weight ratio)

TiO<sub>2</sub>: Titania carrier

### Example 16

When the procedure of Example 11 was repeated, except that the reaction vessel measured 700 mm in inside diameter and 3 m in height and used a catalyst bed 0.79 m in overall height, the actual linear velocity of gas was found to be 0.46 cm/sec and the efficiency of treatment of acetic acid was found to be 91%.

### Example 17

When the procedure of Example 11 was repeated, except that the reaction vessel measured 90 mm in inside diameter and 12 m in height and used six serially arranged catalyst beds each measuring 8 m in height, the actual

linear velocity of gas was found to be 28 cm/sec and the efficiency of treatment of acetic acid was found to be 96.2%. The pressure loss in the catalyst beds conspicuously increased to 7 kg/cm<sup>2</sup>.

5 Example 18

10 In the treatment of Example 11, the liquid was sampled at a position of 30% of the length of the catalyst bed from the inlet side thereof and analyzed to determine the efficiency of treatment. The efficiency was found to be 72% for acetic acid, 88% for acrylic acid, 86% for methacrylic acid, 98% for aldehydes, and 85% for other organic substances.

The claims form part of the disclosure of this specification.



~~WHAT IS CLAIMED IS:~~ The claims defining the invention are as follows:

1. A method for the treatment of the waste water discharging from a (meth)acrylic acid production plant and containing acetic acid and aldehydes by supplying said waste water to a wet oxidation reaction vessel packed with a solid catalyst and operated at a temperature not exceeding 370°C under a pressure enough for said waste water to retain a liquid phase under continued supply of a molecular oxygen-containing gas thereby effecting wet oxidation of the organic substances present in said waste water.
2. A method according to claim 1, wherein said solid catalyst has as a carrier component thereof an oxide containing titanium.
3. A method according to claim 2, wherein said solid catalyst comprises a carrier having as a component thereof an oxide containing titanium and a catalytically active component formed of either a compound of at least one metal selected from the group consisting of manganese, iron, cobalt, nickel, tungsten, copper, cerium, and silver or at least one metal selected from the group consisting of platinum, palladium, rhodium, ruthenium, and iridium, said carrier accounting for a proportion in the range of 75 to 99.95% by weight and said catalytically active component for a proportion in the range of 25 to 0.05% by weight.
4. A method according to claim 3, wherein said solid catalyst has as a catalytically active component thereof at least one metal selected from the group consisting of platinum, rhodium, ruthenium, and palladium and said metal accounts for a proportion in the range of 0.1 to 5% by weight, based on the total amount of said catalyst.
5. A method according to claim 1, wherein said wet oxidation reaction vessel packed with said solid catalyst possesses a heat-exchange ability.
6. A method according to claim 1, wherein the treated water resulting from said wet oxidation of waste water is utilized as a service water for said plant.

7. A method according to claim 1, wherein said supply of said molecular oxygen-containing gas is carried out so that the actual linear velocity of said gas in said catalyst bed is in the range of 0.6 to 20 cm/sec.
8. A method according to claim 1, wherein said waste water from a (meth)acrylic acid production plant contains acetic acid in a concentration in the range of 0.04 to 20% by weight and aldehydes in a combined concentration in the range of 0.02 to 4% by weight.
9. A method according to claim 2, wherein said carrier having a titanium-containing oxide as a component thereof is at least one oxide selected from the group consisting of titania, titania-silica, and titania-zirconia.
10. A method according to claim 9, wherein said oxide is a binary composite oxide consisting of 20 to 90 mol% of titania and 80 to 10 mol% of zirconia.
11. A method according to claim 1, wherein said waste gas from said (meth)acrylic acid production plant has had 50 to 100% of aldehydes thereof already oxidized at a position of 30% of the length of said catalyst bed from the inlet side thereof.
12. A method for the production of (meth)acrylic acid, which comprises subjecting a feed gas containing an olefin of 3 or 4 carbon atoms to gas phase catalytic oxidation, causing the resultant oxidized gas to be absorbed in water by direct contact therewith, separating (meth)acrylic acid from the resultant aqueous solution of said oxidized gas, supplying the resultant waste water containing acetic acid and aldehydes to a wet oxidation reaction vessel packed with a solid catalyst and operated at a temperature not exceeding 370°C under a pressure enough for said waste water to retain a liquid phase under continued supply of a molecular oxygen-containing gas thereby purifying said waste water by wet oxidation of organic substances entrained by said waste water, and cycling the purified waste water to a step for

the absorption of the gas produced by oxidation thereby effecting absorption of said produced gas of oxidation.

13. A method according to claim 12, wherein said solid catalyst has as a carrier component thereof an oxide containing titanium.

14. A method according to claim 13, wherein said solid catalyst comprises a carrier having as a component thereof an oxide containing titanium and a catalytically active component formed of either a compound of at least one metal selected from the group consisting of manganese, iron, cobalt, nickel, tungsten, copper, cerium, and silver or at least one metal selected from the group consisting of platinum, palladium, rhodium, ruthenium, and iridium, said carrier accounting for a proportion in the range of 75 to 99.95% by weight and said catalytically active component for a proportion in the range of 25 to 0.05% by weight.

15. A method according to claim 14, wherein said solid catalyst has as a catalytically active component thereof at least one metal selected from the group consisting of platinum, rhodium, ruthenium, and palladium and said metal accounts for a proportion in the range of 0.1 to 5% by weight, based on the total amount of said catalyst.

16. A method according to claim 12, wherein said wet oxidation reaction vessel packed with said solid catalyst possesses a heat-exchange ability.

17. A method according to claim 12, wherein said supply of said molecular oxygen-containing gas is carried out so that the actual linear velocity of said gas in said catalyst bed is in the range of 0.6 to 20 cm/sec.

18. A method according to claim 12, wherein said waste water from a (meth)acrylic acid production plant contains acetic acid in a concentration in the range of 0.04 to 20% by weight and aldehydes in a combined concentration in the range of 0.02 to 4% by weight.

19. A method according to claim 13, wherein said carrier having a titanium-containing oxide as a component thereof is

at least one oxide selected from the group consisting of titania, titania-silica, and titania-zirconia.

20. A method according to claim 19, wherein said oxide is a binary composite oxide consisting of 20 to 90 mol% of titania and 80 to 10 mol% of zirconia.

21. A method according to claim 12, wherein said waste gas from said (meth)acrylic acid production plant has had 50 to 100% of aldehydes thereof already oxidized at a position of 30% of the length of said catalyst bed from the inlet side thereof.

22. A method for the treatment of waste water substantially as herein described with reference to the examples and/or the accompanying drawings.

23. The product of the method of any one of claims 1 to 21.

24. The steps, features or integers disclosed in the accompanying specification or drawings, individually or in any combination.

DATED this 3rd December, 1990

SMITH SHELSTON BEADLE

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Patent Attorneys for the Applicant:

NIPPON SHOKUBAI KAGAKU KOGYO CO., LTD.

FIG. 1

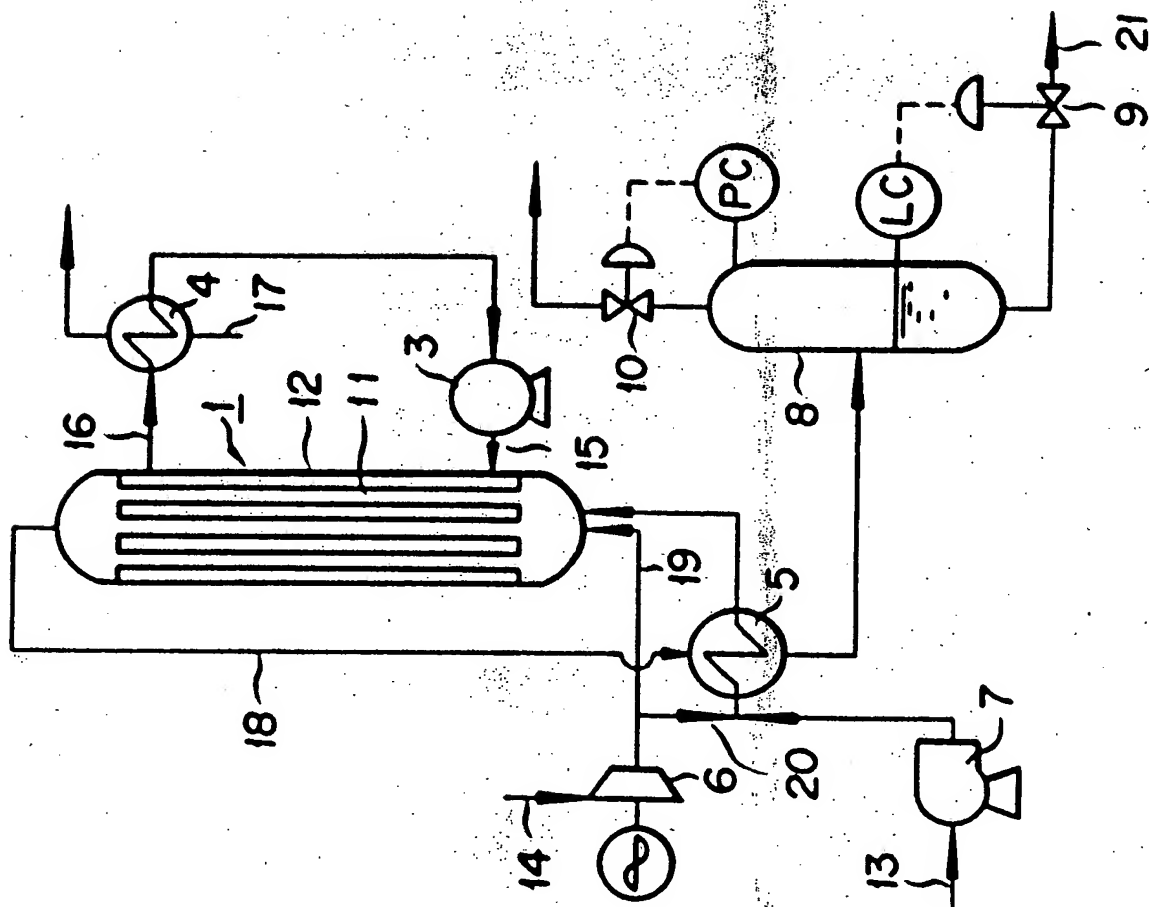
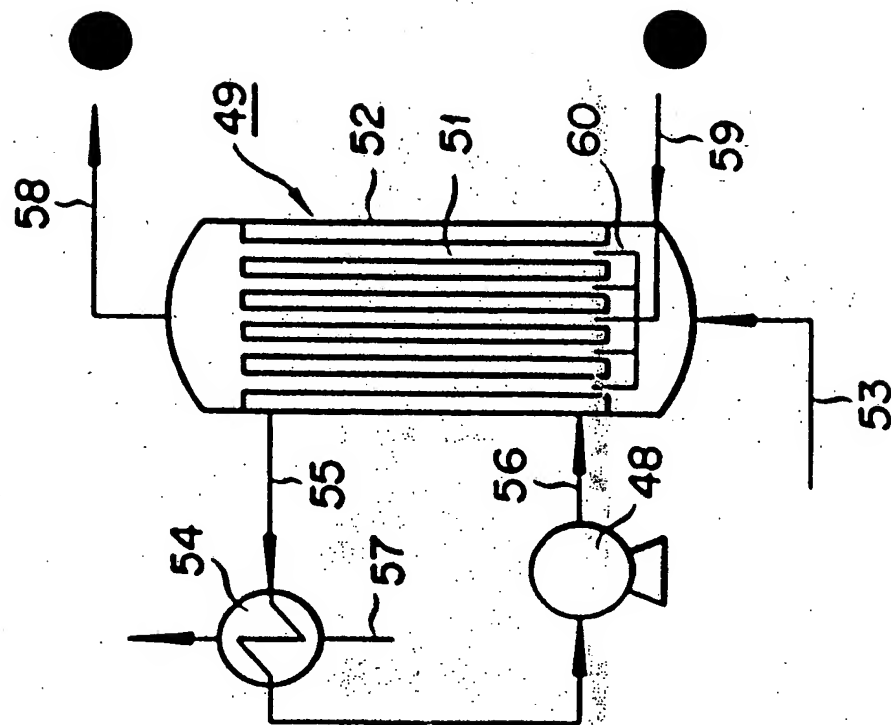


FIG. 3



# FIG. 2

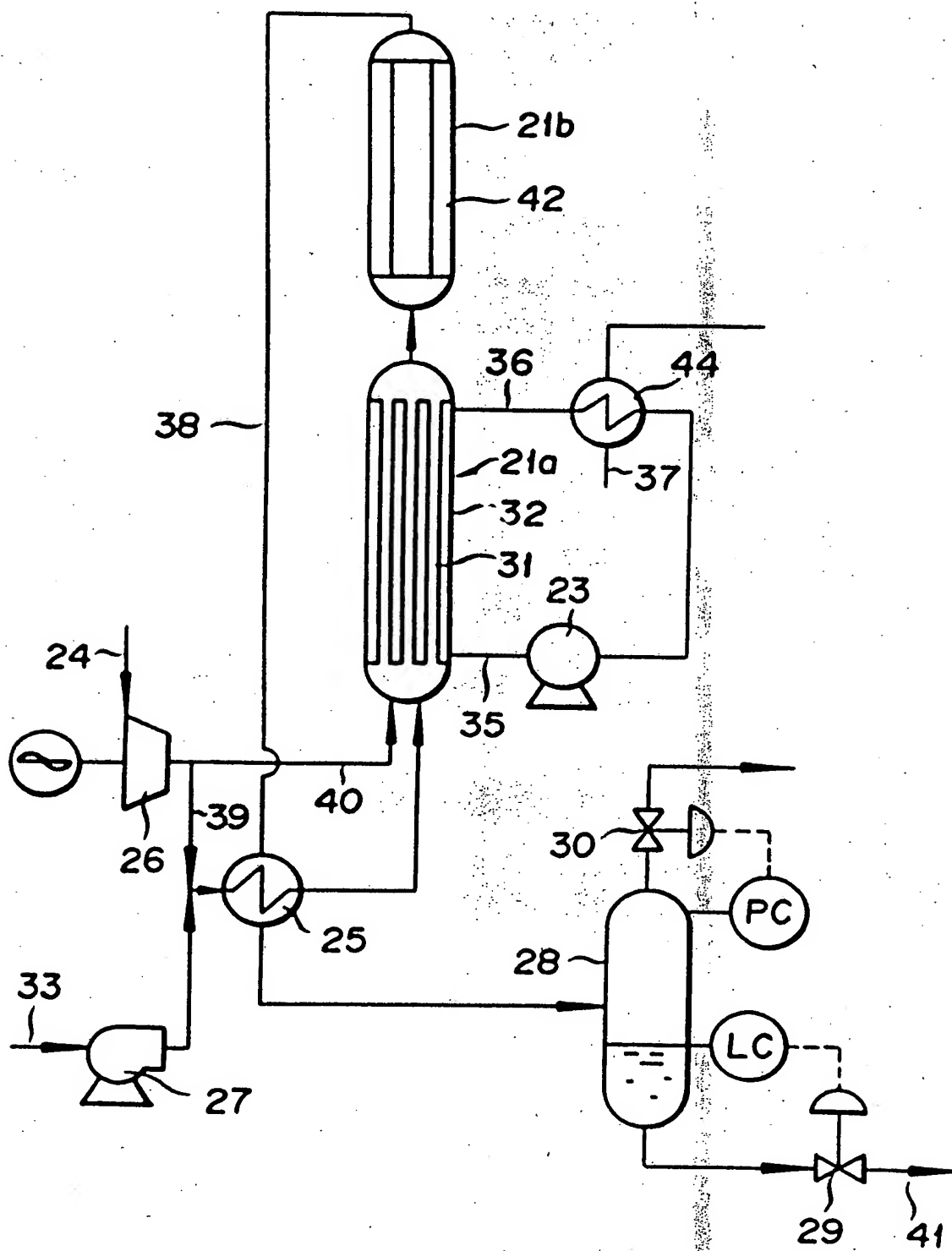
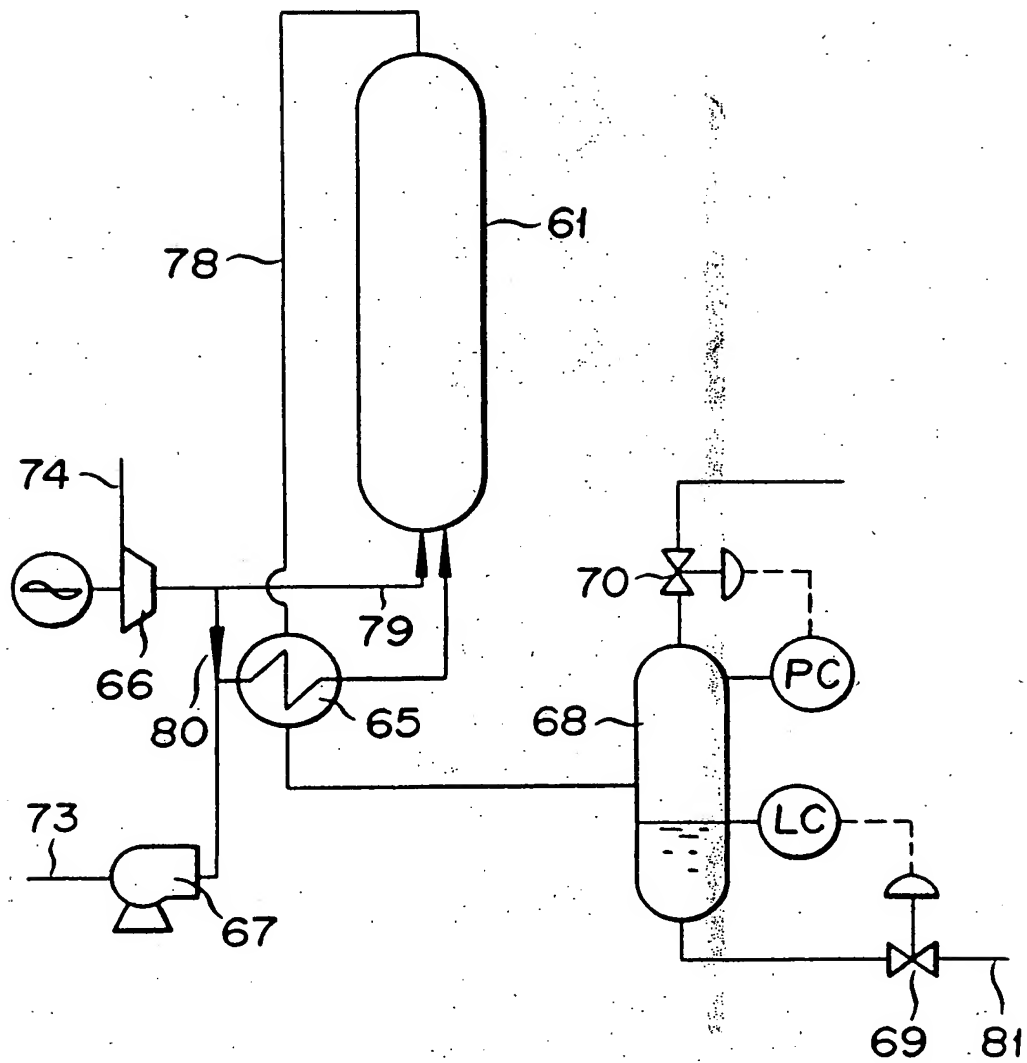


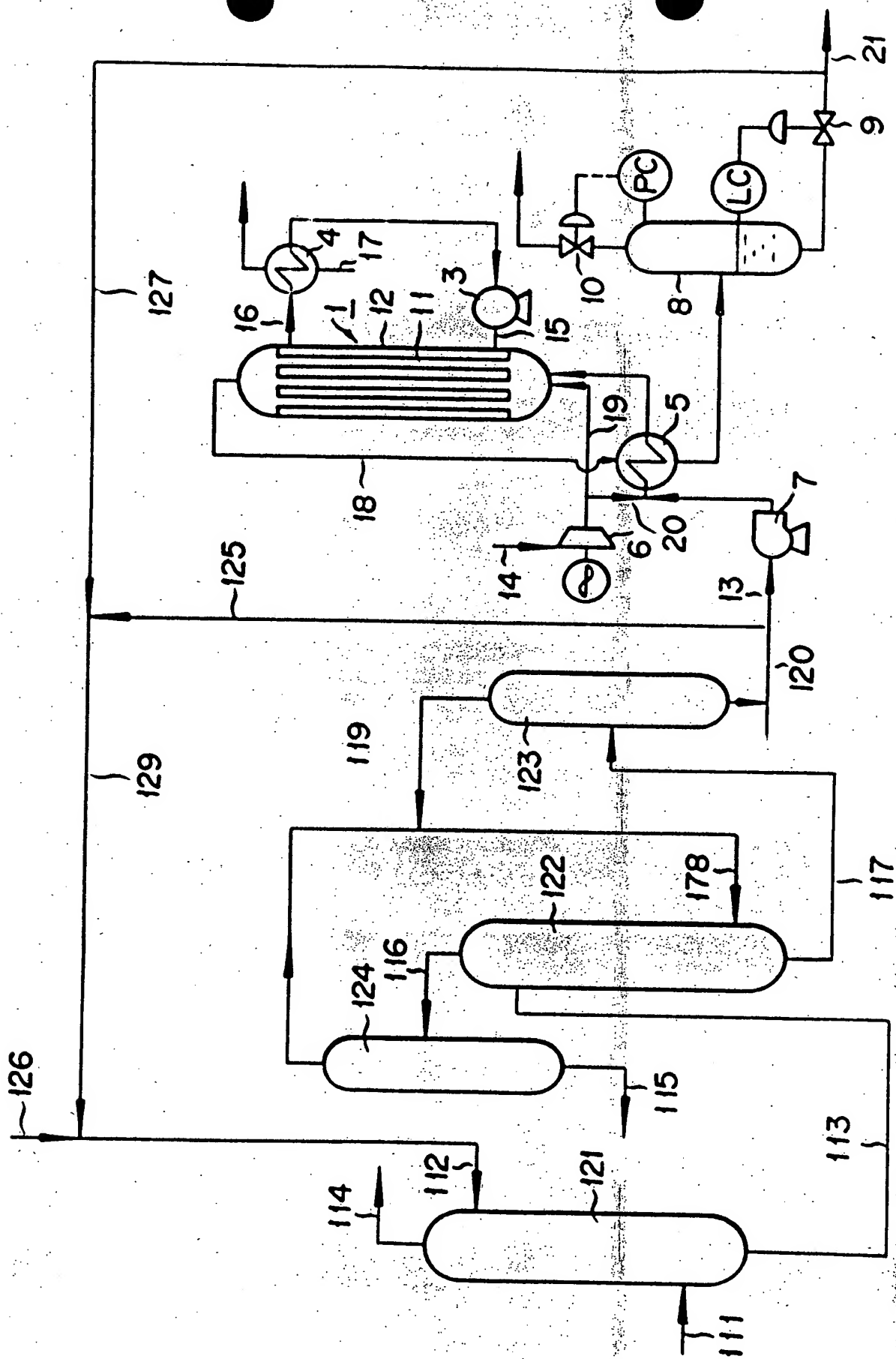
FIG. 4



[illegible]



# FIG. 6



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